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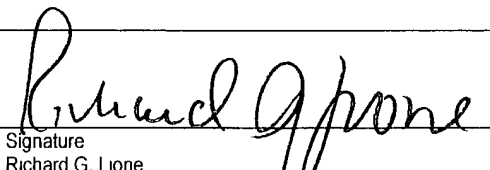
Date of Deposit January 14, 2002



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JC03 Rec'd PCT/PTO 14 JAN 2002

FORM PTO-1390 (REV. 5-93)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	CASE NO. 5404-17
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/031290
INTERNATIONAL APPLICATION NO. PCT/JP00/04711	INTERNATIONAL FILING DATE July 13, 2000	PRIORITY DATE CLAIMED July 14, 1999	
TITLE OF INVENTION REGENERATED COLLAGEN FIBER WITH EXCELLENT HEAT RESISTANCE			
APPLICANT(S) FOR DO/EO/US Masahiro Ueda, Yoshihiro Makihara, Takashi Ueda, and Kunihiro Matsumura			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none">1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 3712. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 3713. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).<ol style="list-style-type: none">a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).<ol style="list-style-type: none">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).b. <input type="checkbox"/> have been transmitted by the International Bureau.c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.d. <input type="checkbox"/> have not been made and will not be made.8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)) and/or amendments under Article 34.			
Items 11. to 16. Below concern other document(s) or information included:			
<ol style="list-style-type: none">11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.14. <input type="checkbox"/> A substitute specification.15. <input type="checkbox"/> A change of power of attorney and/or address letter.16. <input type="checkbox"/> Other items or information:			

531 Rec'd PCT/PTT 14 JAN 2002

U.S. APPLICATION NO. 10/031290 <small>(If known, see 37 CFR 1.50)</small>		INTERNATIONAL APPLICATION NO. PCT/JP00/04711		CASE NO. 5404-17			
17. <input checked="" type="checkbox"/> The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO\$890 00 International preliminary examination fee paid to USPTO (37 CFR 1.492(a)(1))\$710 00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.492(a)(2))\$740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.492(a)(3)) paid to USPTO.....\$1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100 00 <div style="text-align: center;">ENTER APPROPRIATE BASIC FEE AMOUNT</div>				CALCULATIONS		PTO USE ONLY	
Surcharge of \$130 00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).							
Claims	Number Filed	Number Extra	Rate				
Total Claims	6- 20 =	0	x \$ 18.00				
Independent Claims	3- 3 =	0	x \$ 84.00				
Multiple dependent claim(s) if Applicable)		0	+ \$280 00				
TOTAL OF ABOVE CALCULATIONS =				\$890			
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)							
SUBTOTAL =				\$890			
Surcharge of \$130.00 for furnishing the English translation later than the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$			
TOTAL NATIONAL FEE=				\$890			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +							
TOTAL FEES ENCLOSED=				\$890			
				Amount to be refunded	\$		
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a. <input checked="" type="checkbox"/> A check in the amount of \$890 to cover the above fees is enclosed b. <input type="checkbox"/> Please charge my Deposit Account No. 23-1925 in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-1925 A duplicate copy of this sheet is enclosed							
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.							
Send All Correspondence to. Brinks Hofer Gilson & Lione P.O. Box 10395 Chicago, IL 60610			 Signature Richard G. Lione Name 19,795 Registration Number				

10/031290

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Date of Deposit: January 14, 2002

Patent

Our Case No. 5404/17

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PCT RECEIVING OFFICE

In re Application of:)
Masahiro Ueda et al.)
International Application)
No. PCT/JP00/04711)
Filed: July 13, 2000)
For: REGENERATED COLLAGEN)
FIBER WITH EXCELLENT)
HEAT RESISTANCE)

PRELIMINARY AMENDMENT

The Commissioner for Patents
Box PCT
Washington, D.C. 20231

Dear Sir:

Preliminary to examination of the subject application, please amend the above-identified application as follows:

IN THE SPECIFICATION

Page 1, after the title, insert the following paragraph:

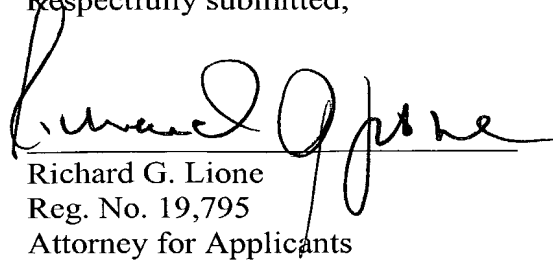
"RELATED APPLICATIONS

This application is a nationalization of PCT application PCT/JP00/04711 filed July 13, 2000. This application claims priority from the PCT application and Japan Application Serial No. Hei 11-200294 filed July 14, 1999."

REMARKS

The specification is amended to make record therein of the priority claims.

Respectfully submitted,



Richard G. Lione
Reg. No. 19,795
Attorney for Applicants

Date: Jan. 14, 2002

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SPECIFICATION

REGENERATED COLLAGEN FIBER WITH EXCELLENT HEAT RESISTANCE

Technical Field

This invention relates to a regenerated fiber. More particularly, it relates to a regenerated collagen fiber with excellent heat resistance, which can suitably be used for human hair or fur, or as thread to be wound by hand.

Background Art

Among the protein fibers, the regenerated collagen fiber exhibits a high mechanical strength like silk, and, thus, has so far been used in various fields. Particularly, the regenerated collagen fiber is a protein fiber maintaining a characteristic molecular structure derived from collagen and, thus, is close in drape, luster and feel to the human hair that is a natural protein fiber having complex fine structure. Such being the situation, it has been attempted to use the regenerated collagen fiber as human hair or an animal hair-like fiber such as a fur (for example, Japanese Patent Laid-Open No. 168628/1998 and Japanese Patent Laid-Open No. 168629/1998).

In general, the skin or bone of an animal is used as a raw material of the regenerated collagen fiber. The

regenerated collagen fiber can be produced by treating these raw materials with an alkali or an enzyme to obtain a water-soluble collagen, followed by extruding and spinning the water-soluble collagen in an aqueous solution of an inorganic salt. Since the regenerated collagen fiber thus obtained is soluble in water, some treatments are applied thereto in order to impart resistance to water to the collagen fiber. As a method for making the regenerated collagen fiber insoluble in water, there have been known methods of treating the water-soluble collagen fiber with an aldehyde compound such as formaldehyde or glutaric aldehyde; methods of treating the water-soluble collagen fiber with metal salts such as various chromium salts, aluminum salts or zirconium salts; methods of treating the water-soluble collagen fiber with an epoxy compound; and methods of treating the regenerated collagen fiber with a combination of the above-described methods (for example, Japanese Patent Laid-Open No. 173161/1994).

However, being produced from collagen, the fiber produced by these methods has a lower heat resistance than that of human hair or animal hair containing keratin as a major component, and is susceptible to thermal damages (contraction in length, curling or hardening of hair tips) upon styling with a hair iron or dryer, thus not being satisfactory in view of hair-dressing properties (the term "styling" as used herein means to impart a desired form to human hair by thermal

treatment in a beauty parlor or at home).

An object of the invention is to provide a regenerated collagen fiber with excellent heat resistance, which is less apt to be damaged even in styling with a hair iron or dryer.

Disclosure of the Invention

Under such circumstances, as a result of intensive investigations, the inventors have found that the regenerated collagen fiber with excellent heat resistance can be obtained by compounding 1 to 100 parts by weight of a thermoplastic resin with 100 parts of collagen.

That is, the invention is a regenerated collagen fiber comprising 100 parts by weight of collagen and 1 to 100 parts by weight of a thermoplastic resin, and the thermoplastic resin is preferably one obtained by polymerizing at least one member selected from the group consisting of alkyl acrylate monomers, alkyl methacrylate monomers, acrylic acid, methacrylic acid, vinyl cyanide monomers, aromatic vinyl monomers, and halogenated vinyl monomers.

Best Mode for Carrying Out the Invention

As a raw material of collagen to be used in the invention, split leather is preferred. The split leather can be obtained from a fresh raw hide or a salted hide of animals such as cows. Such split leather mostly comprises insoluble collagen fibers,

and is usually used after removing therefrom flesh portions attached thereto to form a network and a salt component used for preventing the leather from becoming putrid or deteriorated.

Split leather under this condition still contains impurities, for example, lipids such as glyceride, phospholipid and free fatty acids, and proteins other than collagen, such as sugar proteins and albumin. Since these impurities greatly affect adversely the spinning stability in forming fiber, the quality such as luster and elongation of the resultant fiber, and the odor, it is desirable to remove these impurities in advance by, for example, dipping split leather in lime to hydrolyze the fat components so as to loosen the collagen fiber, followed by applying a conventional hide treatment such as an acid-alkali treatment, an enzyme treatment and a solvent treatment.

The thus treated insoluble collagen is subjected to a solubilizing treatment in order to cut the crosslinking peptide portion. As such solubilizing treatment, there may be employed an alkali solubilizing method or an enzyme solubilizing method, which are commonly employed as a method of the solubilizing treatment.

In the case of employing the alkali solubilizing method, it is desirable to neutralize the solubilized collagen with an acid such as hydrochloric acid. It is also possible to

employ the method described in Japanese Patent Publication No. 15033/71 as an improved alkali solubilizing method.

The enzyme solubilizing method is advantageous in that it is possible to obtain a regenerated collagen having a uniform molecular weight and, thus, the enzyme solubilizing method can be favorably employed in the invention. As such enzyme solubilizing method, the method described in, for example, Japanese Patent Publication No. 25829/68 or Japanese Patent Publication No. 27513/68 can be employed in the invention. Incidentally, it is possible in the invention to employ in combination both the alkali solubilizing method and the enzyme solubilizing method.

Where additional treatments such as pH adjustment, salting-out, water wash and treatment with a solvent are applied to the collagen to which the solubilizing treatment has been applied, it is possible to obtain a regenerated collagen fiber having an excellent quality. Thus, it is desirable to apply these additional treatments to the solubilized collagen.

The solubilized collagen leather pieces thus obtained is dissolved in an acidic aqueous solution having the pH value adjusted to 2 to 4.5 with hydrochloric acid, acetic acid, lactic acid or the like to provide a stock solution of a predetermined concentration of, for example, about 1 to about 15% by weight, preferably about 2 to about 10% by weight, thus an aqueous

solution of collagen being prepared.

In the invention, a thermoplastic resin is added to either a solubilized collagen leather pieces before the acid such as hydrochloric acid, acetic acid or lactic acid being added thereto or to an aqueous solution of collagen to which the acid has been added, in an amount of 1 to 100 parts by weight per 100 parts by weight of collagen.

The amount of the thermoplastic resin to be compounded is preferably 3 to 80 parts by weight, more preferably 5 to 50 parts by weight. In case where the amount is less than 1 part by weight, effect of improving heat resistance tends to become insufficient whereas, in case where more than 100 parts by weight, there tends to result a fragile fiber which is difficult to handle, though heat resistance being improved.

Mechanism how heat resistance is improved by compounding the thermoplastic resin is not clear, but may be presumed as that thermoplastic resin particles existing inside the regenerated collagen fiber form some structure within the fiber which functions to inhibit deformation such as contraction of collagen molecules upon heating with a hair iron or the like.

As the thermoplastic resin to be compounded, there may preferably be used those resins which are prepared by homopolymerizing or copolymerizing two or more of the monomers such as alkyl acrylate monomers (alkyl moiety containing

preferably 1 to 12, more preferably 1 to 6, carbon atoms) (e.g., methyl acrylate, ethyl acrylate, butyl acrylate or octyl acrylate); alkyl methacrylate monomers (alkyl moiety containing preferably 1 to 6, more preferably 1 to 4, carbon atoms) (e.g., methyl methacrylate or ethyl methacrylate); acrylic acid or methacrylic acid; vinyl cyanide monomers (e.g., acrylonitrile or methacrylonitrile); aromatic vinyl monomers (e.g., styrene or α -methylstyrene); and vinyl halide monomers (e.g., vinyl chloride or vinyl bromide). In addition to the monomers, crosslinking agents such as divinylbenzene, monoethylene glycol dimethacrylate and polyethylene glycol dimethacrylate may be used alone or as a mixture of two or more. Of these alkyl acrylate monomers, alkyl methacrylate monomers and aromatic vinyl monomers are preferred as the monomers for producing the resin to be compounded, with a combination of an alkyl acrylate monomer and an alkyl methacrylate monomer, and a combination of an alkyl acrylate monomer and an aromatic vinyl monomer being more preferred. In particular, a combination of methyl methacrylate and butyl acrylate and a combination of styrene and butyl acrylate are preferred.

The thermoplastic resin has a glass transition temperature of 0°C to 120°C, preferably 30°C to 100°C, more preferably 30°C to 80°C. The term "glass transition temperature" as used herein means a middle glass transition temperature of a peak measured at a temperature-raising rate

of 10°C/min according to the method described in JISK7121. In case where the glass transition temperature is less than 0°C, the thermoplastic resin particles are liable to agglomerate upon compounding, leading to formation of large masses which reduce strength of resultant regenerated collagen fiber containing them. On the other hand, in case where the glass transition temperature exceeds 120°C, effects obtained by compounding the thermoplastic resin tend to be weakened.

Further, the thermoplastic resin particles have a particle size of preferably 5 μm or less, more preferably 1 μm or less, still more preferably 0.5 μm or less. In case where the particle size exceeds 5 μm , there tends to result a fragile fiber. As the thermoplastic resin particles, powder pulverized with a mill or latex particles prepared by emulsion polymerization or suspension polymerization may be used. In particular, latex particles obtained by emulsion polymerization are uniform in particle size and has a good stability in water and, therefore, is easy to handle, thus being preferably used.

In the case of compounding the thermoplastic resin particles with the solubilized collagen, an acid is further added after compounding the thermoplastic resin particles, followed by well stirring the mixture in a kneader or the like for 2 hours or longer, preferably 5 hours or longer, to prepare an aqueous solution of collagen wherein the particles are

uniformly dispersed. In addition, in the case of compounding the thermoplastic resin with an aqueous solution of collagen, the mixture is well stirred for 1 hour or longer in a kneader or the like to uniformly disperse the thermoplastic resin particles in the aqueous solution of collagen. These procedures are conducted at a temperature of preferably 25°C or lower. In case where the temperature is higher than 25°C, the aqueous solution of collagen might be denatured, leading to difficulty in stable production of fiber. Further, in the case of using a thermoplastic resin having a glass transition temperature of lower than 25°C, it is desirable to conduct the treatment at a temperature not higher than the glass transition temperature of the added resin in order to prevent agglomeration of the resin particles.

Additionally, the thus obtained aqueous solution of collagen may, if necessary, be subjected to a defoaming procedure by stirring under reduced pressure or a filtering procedure to remove large-sized foreign matter.

Further, to the thus obtained aqueous solution of the solubilized collagen may, if necessary, be added additives such as a stabilizer and a water-soluble high-molecular compound in proper amounts for the purpose of, for example, improving mechanical strength, resistance to water and to heat, luster and spinning properties, preventing coloration and imparting antiseptic properties.

The aforesaid aqueous solution of the solubilized collagen is then discharged through, for example, a spinning nozzle or slit, and the discharged solution is dipped in an aqueous solution of an inorganic salt so as to obtain a regenerated collagen fiber. As the aqueous solution of an inorganic salt, there may be used, for example, an aqueous solution of a water-soluble inorganic salt such as sodium sulfate, sodium chloride or ammonium sulfate. Usually, the inorganic salt concentration in the aqueous solution is adjusted to 10 to 40% by weight.

PH of the aqueous solution of the inorganic salt is desirably adjusted to 2 to 13, preferably 4 to 12, by adding a metal salt such as sodium borate or sodium acetate or hydrochloric acid, acetic acid or sodium hydroxide to the aqueous solution. In case where the pH value is smaller than 2 or exceeds 13, the peptide linkage of collagen is likely to be hydrolyzed, sometimes resulting in failure to obtain a desired fiber. Also, it is desirable for the temperature of the aqueous solution of the inorganic salt, which is not particularly limited in the present invention, to be adjusted in general, for example, to 35°C or lower. In case where the temperature of the aqueous solution is higher than 35°C, the soluble collagen is denatured or the mechanical strength of the spun fiber is lowered, with the result that it becomes difficult to manufacture fiber thread with a high stability.

The lower limit of the temperature range is not particularly limited in the invention. It suffices to adjust the lower limit of the temperature appropriately in accordance with the solubility of the inorganic salt.

Then, these fibers are commonly treated with a crosslinking agent for improving resistance to water. As methods for treating with a crosslinking agent, there are illustrated, for example, a method of previously adding a crosslinking agent to the aqueous solution of an inorganic salt, and conducting the water resistance-imparting treatment simultaneously with spinning, and a method of subjecting a spun regenerated collagen fiber to a treatment with a crosslinking agent.

As the crosslinking agent, there are illustrated, for example, monoaldehydes such as formaldehyde, acetaldehyde, methyl glyoxal, acrolein, and crotonaldehyde; dialdehydes such as glyoxal, malondialdehyde, succindialdehyde, glutaraldehyde, and dialdehyde starch; alkylene oxides such as ethylene oxide and propylene oxide; halogenated alkylene oxides such as epichlorohydrin; epoxy compounds including glycidyl ethers of aliphatic alcohol, glycol and polyols, and glycidyl esters of monocarboxylic acid, dicarboxylic acid, and polycarboxylic acid; N-methylol compounds derived from urea, melanin, acrylamide acrylic acid amide and polymers thereof; water soluble polyurethanes prepared by introducing

isocyanate into a polyol or a polycarboxylic acid, followed by adding sodium hydrogen sulfite; triazine derivatives such as monochlorotriazine and dichlorotriazine; sulfate ester of oxyethyl sulfone or derivatives of vinyl sulfone; trichloropyridine derivatives; dichloroquinoxaline derivatives; N-methylol derivatives; isocyanate compounds; phenol derivatives; aromatic compounds having a hydroxyl group represented by tannin; and inorganic crosslinking agents of metal salts wherein a cation of metal such as aluminum, chromium, titanium or zirconium is combined with an anion such as sulfate ion, nitrate ion, halide ion represented by chloride ion or hydroxyl ion. However, the crosslinking agents to be used in the invention are not limited only to these crosslinking agents, and other crosslinking agents may also be used which can reduce contraction with hot water, water absorption or swelling degree in water of the regenerated collagen and can make the regenerated collagen fiber insoluble in water. Additionally, water-insoluble crosslinking agents may be used as an emulsion or a suspension. These crosslinking agents may usually be used alone or as a mixture of two or more of them.

Of these crosslinking agents, metal salts can impart a particularly excellent heat resistance to the regenerated collagen. In particular, use of an aluminum salt realizes remarkable effects by the addition of the thermoplastic resin, thus being particularly preferred in the invention.

Further, in the invention, water wash, oiling and drying are applied as required to the regenerated collagen fiber.

Drying is usually conducted in a hot air convection dryer. The regenerated collagen fiber is liable to contract upon being dried, and it is extremely difficult for the once deformed collagen fiber to be formed into a desired form. Thus, in the invention, drying is conducted in a state wherein the fiber is fixed at both ends under tension or in a stretched state wherein a load is applied to both ends of the fiber so that the contraction ratio of the fiber after drying becomes 30% or less, preferably 20% or less, still more preferably 10% or less without being broken. In case where the contraction ratio of the fiber thread after drying exceeds 30%, complicated unevenness tends to be formed on the surface of the fiber to cause detrimental influences on touch feel. The atmospheric temperature within the dryer is not particularly limited, but a temperature of not lower than the glass transition temperature of the added thermoplastic resin is preferred because the effect of improving heat resistance is more remarkable. This may be attributed to that a continuous structure is formed within the regenerated collagen fiber by welding of the added thermoplastic resin particles to each other, which serves to improve heat resistance. Further, as to the atmospheric temperature within the dryer, it is preferably 100°C or lower, more preferably 90°C or lower,

because, in case where it is too high, the fiber might be colored or denatured. Drying time is longer than that which is required to completely dry the fiber and shorter than that at which decoloration of the fiber becomes serious.

The water wash is intended to prevent precipitation of an oiling agent caused by a salt and to prevent the salt from being precipitated from the regenerated collagen fiber during drying within a drying machine. In case where the salt is precipitated, the regenerated collagen fiber is cut or broken, the formed salt scatters within the drying machine so as to be attached to the heat exchanger within the drying machine, leading to a low heat transfer coefficient. Also, the oiling is effective for preventing the fiber from hanging up in the drying step and for improving the surface state of the regenerated collagen fiber.

The thus obtained regenerated collagen fiber containing the thermoplastic resin has an excellent heat resistance, and enables to conduct styling with a hair iron or dryer with maintaining drape the natural protein fiber has, thus being more favorably usable as a substitute or a piece for improving human hair and animal hair.

The invention is now described in more detail by reference to Examples which, however, do not limit the invention in any way.

Additionally, in the invention, heat resistance of the

regenerated collagen fiber is evaluated by measuring contraction ratio of the fiber and damage of the fiber at its tip upon applying thereto a hair iron, with these being taken as representative data for heat resistance. Fineness of the fiber is represented in terms of d (denier) and dtex (decitex).

Glass transition temperature and particle size of the thermoplastic resin used in Examples and heat resistance of the regenerated collagen fiber prepared in Examples upon applying a hair iron were measured according to the following methods.

(1) Glass transition temperature of the thermoplastic resin particles:

A thermoplastic resin latex obtained by emulsion polymerization was dried at 25°C for 48 hours, then kept in a 25°C vacuum dryer for 24 hours to obtain powder from which moisture was completely removed. About 10 mg of the powder was taken out according to the method described in JISK7121, and a middle-point glass transition temperature of the peak was read off, the peak being measured using differential scanning calorimeter (made by Seiko Denshi Kogyo K.K.; DSC-220C) under the conditions of -50°C in initial temperature and 10°C/min in temperature-raising rate.

(2) Particle size of the thermoplastic resin particles:

A thermoplastic resin latex obtained by emulsion polymerization was dried at 25°C for 48 hours to obtain powder,

and this powder was observed using a scanning type electron microscope (made by Hitachi, Ltd.; S-800) to measure the particle size.

(3) Heat resistance upon applying a hair iron:

The following procedures were conducted in an atmosphere of $20 \pm 2^\circ\text{C}$ in temperature and $65 \pm 2\%$ in relative humidity.

After well opening the fibers, they were bunched in a length of 250 mm. To the bunch of fibers was lightly applied a hair iron (Perming Iron; made by Hakko Kogyo K.K.) heated to a varying temperature, and the hair iron was slid once rapidly (2 sec/slide) along the upper surface and the lower surface to evaporate moisture on the surface of the fibers. Then, the bunch of fibers was nipped with the iron, and the iron was slid from the base to the top of the bunch of fibers in 5 seconds. After this procedure, contraction ratio of the fiber bunch and the shrank state of the fiber at its tip were examined. Contraction ratio was determined from the following formula [1]

$$\text{Contraction ratio} = [(L - L_0) / L] \times 100 \quad [1]$$

wherein L represents a length of the fiber bunch before being treated with the iron, and L_0 represents a length of the fiber bunch after being treated with the iron (in case where wave is formed in the fiber bunch upon treating with the iron, the length being measured by straightening the fiber bunch).

Hair iron heat resistance was described in terms of a

hair iron heat-resistant temperature which was measured as the maximum temperature at which contraction ratio was 5% or less and no shrinkage was observed. The hair iron temperature was raised by 10°C, and the fiber bunch was changed to a new fiber bunch upon measuring at each different temperature.

Example 1

Emulsion polymerization was conducted using 60 parts by weight of styrene, 40 parts by weight of butyl acrylate, and 1 part by weight of a surfactant of sodium laurylsulfate to obtain a latex containing 20% by weight of a solid component comprising resin particles having a glass transition temperature of 41°C and a particle size of 0.1 μm . Further, 45 g of the latex (resin: 9 g) was mixed with 1200 g (collagen content: 180 g) of leather pieces obtained by solubilizing split leather with an alkali. Then, an aqueous solution of lactic acid and water were added thereto in a definite amount, and the mixture was stirred in a kneader (made by K.K. Irie Shokai; Model PNV-5; hereinafter the same) to prepare a stock solution having a pH adjusted to 3.5 and a solid component (comprising collagen and the thermoplastic resin) concentration adjusted to 7.5% by weight. Thereafter, the solution was subjected to a defoaming treatment by stirring under a reduced pressure (using a stirring defoamer, model 8DMV, made by Dalton Corporation) for one hour, followed by transferring the treated solution to a piston type spinning

stock solution tank. The solution thus transferred was further allowed to stand under a reduced pressure to defoam. Then, the stock solution was extruded by a piston, followed by transferring a predetermined amount of the extruded solution by a gear pump and subsequently filtering the extruded solution through a sintered filter of 10 μ m in pore size. Further, the filtered extrudate was passed through a spinning nozzle having 300 pores each pore having a pore diameter of 0.30 mm and a pore length of 0.5 mm so as to discharge the filtered extrudate at a spinning rate of 5 m/min into a coagulating bath of 25°C in temperature containing 20% by weight of sodium sulfate and having the pH value adjusted to 11 with boric acid and sodium hydroxide.

Then, the resultant regenerated collagen fiber was dipped in 16.5 kg of an aqueous solution containing 1.7% by weight of epichlorohydrin, 0.09% by weight of 2,4,6-tris(dimethylaminomethyl)phenol, 0.009% by weight of salicylic acid and 13% by weight of sodium sulfate at 25°C for 24 hours.

After washing the resultant collagen fiber with a flowing water for one hour, it was dipped in 16.5 kg of an aqueous solution containing 6% by weight of basic aluminum chloride (made by Nihon Seika K.K.; Bercotan AC-P; hereinafter the same) and 5% by weight of sodium chloride at 30°C for 12 hours, followed by washing the resultant fiber with a flowing water

for 2 hours.

Subsequently, the fiber was dipped in a bath filled with an oily agent consisting of an emulsion of an amino-modified silicone and PLURONIC polyether antistatic agent so as to allow the oily agent to adhere to the fiber, then dried under tension in a hot air convection dryer (TABAI ESPEC CORP; PV-221; hereinafter the same) whose temperature was set to 60°C with fixing one end of the fiber bunch and applying a load of 0.04 g per d (1.1 dtex). As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 160°C.

Example 2

The same procedures as in Example 1 were conducted except for changing the amount of latex to 90 g (resin: 18 g). As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 170°C.

Example 3

The same procedures as in Example 1 were conducted except for changing the amount of latex to 270 g (resin: 54 g). As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 180°C.

Example 4

Emulsion polymerization was conducted using 80 parts by weight of methyl methacrylate, 20 parts by weight of butyl acrylate, and 1 part by weight of a surfactant of sodium

laurylsulfate to obtain a latex containing 20% by weight of a solid component comprising resin particles having a glass transition temperature of 73°C and a particle size of 0.1 μm .

90 g of the latex (resin: 18 g) was mixed with 1200 g (collagen content: 180 g) of leather pieces obtained by solubilizing split leather of a cattle with an alkali. Subsequent procedures were conducted in the same manner as in Example 1 except for changing the temperature of the hot air convection drying machine to 85°C. As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 160°C.

Example 5

The same procedures as in Example 4 were conducted except for changing the amount of latex to 180 g (resin: 36 g). As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 170°C.

Example 6

The same procedures as in Example 5 were conducted except for changing the temperature of the hot air convection drying machine to 60°C. As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 160°C.

Example 7

The same procedures as in Example 2 were conducted except for conducting the insolubilizing treatment by dipping the

regenerated collagen fiber in a 25°C aqueous solution containing 15% by weight of sodium sulfate and 0.5% by weight of formaldehyde (pH being adjusted to 9 with boric acid and sodium hydroxide) for 15 minutes in place of the treatment with epichlorohydrin. As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 180°C.

Comparative Example 1

The same procedures as in Example 1 were conducted except for not mixing the latex. As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 140°C, which is lower than that obtained by adding the thermoplastic resin and subjecting to the same crosslinking method.

Comparative Example 2

The same procedures as in Example 1 were conducted except for changing the amount of latex to 1350 g (resin: 270 g). The resultant regenerated collagen fiber was so fragile that it suffered fiber breakage upon drying and not being taken out as thread.

Comparative Example 3

The same procedures as in Example 7 were conducted except for not mixing the latex. As a result of measuring iron heat resistance, the hair iron heat resistance temperature was measured to be 160°C, which is lower than that obtained by adding

the thermoplastic resin and subjecting to the same crosslinking method.

Data obtained in Examples and Comparative Examples are shown in Table 1.

Table 1

		Compounded Thermoplastic Resin				Regenerated Collagen Fiber		
		Formulation (parts by weight)	Glass Transition Temperature (°C)	Particle Size (μ m)	Amount Per 100 Parts of Collagen (parts by weight)	Crosslinking Method	Drying Temperature (°C)	Hair Iron Heat Resistant Temperature (°C)
Example	1	ST 60 BA 40	41	0.1	5	ECH/AL	60	160
	2	ditto.	ditto.	ditto.	10	ditto.	ditto.	170
	3	ditto.	ditto.	ditto.	30	ditto.	ditto.	180
	4	MMA 80 BA 20	73	ditto.	10	ditto.	85	160
	5	ditto.	ditto.	ditto.	20	ditto.	ditto.	170
	6	ditto.	ditto.	ditto.	20	ditto.	60	160
	7	ST 60 BA 40	41	ditto.	10	FA/AL	ditto.	180
Comp. Ex	1	—	—	—	—	ECH/AL	ditto.	140
	2	ST 60 BA 40	41	0.1	150	ditto.	ditto.	Measurement being impossible due to serious fiber breakage
	3	—	—	—	—	FA/AL	ditto.	160

Formulation of added resin: ST: styrene; BA: butyl acrylate; MMA: Methyl methacrylate;

Method of crosslinking the regenerated collagen fiber: ECH: epichlorohydrin; FA: formaldehyde

AL: Basic aluminum chloride

It is seen from the results that heat resistance of the regenerated collagen fiber can be improved by incorporating the thermoplastic resin.

Industrial Applicability

The invention is a method for improving heat resistance of the regenerated collagen fiber, which makes the regenerated collagen fiber into an extremely excellent product to be used as a substitute of human hair, for example, wig or hair piece, or head-decorating products such as doll hair.

CLAIMS

1. A regenerated collagen fiber, which comprises 100 parts by weight of collagen and 1 to 100 parts by weight of a thermoplastic resin.
2. The regenerated collagen fiber as described in claim 1, wherein the thermoplastic resin is one obtained by polymerizing at least one member selected from the group consisting of alkyl acrylate monomers, alkyl methacrylate monomers, acrylic acid, methacrylic acid, vinyl cyanide monomers, aromatic vinyl monomers and halogenated vinyl monomers.
3. The regenerated collagen fiber as described in claim 1, wherein the thermoplastic resin has a glass transition temperature of 0°C to 120°C.
4. The regenerated collagen fiber as described in claim 1, wherein the thermoplastic resin has a glass transition temperature of 30°C to 100°C.
5. A process for producing a regenerated collagen fiber, which comprises mixing 1 to 100 parts by weight of a thermoplastic resin with 100 parts by weight of collagen, and

drying the mixture at a temperature of 100°C or lower than that.

6. A process for producing a regenerated collagen fiber, which comprises mixing 1 to 100 parts by weight of a thermoplastic resin with 100 parts by weight of collagen, and drying the mixture at a temperature of 100°C or lower than that so that contraction ratio of the fiber is 30% or less.

ABSTRACT

A regenerated collagen fiber which comprises 100 parts by weight of collagen and 1 to 100 parts by weight of a thermoplastic resin and has such excellent heat resistance that it is less apt to be thermally damaged even in styling with a hair iron or dryer. The thermoplastic resin is one obtained by polymerizing at least one member selected from the group consisting of alkyl acrylate monomers, alkyl methacrylate monomers, acrylic acid, methacrylic acid, vinyl cyanide monomers, aromatic vinyl monomers and halogenated vinyl monomers.

Our Case No. 5404-17

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Combined Declaration And Power Of Attorney

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or as joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: REGENERATED COLLAGEN FIBER WITH, the specification of which EXCELLENT HEAT RESISTANCE

(check one) _____ is attached hereto.

_____ was filed on _____
as U.S. Application Serial No. _____

X _____ was filed on July 13, 2000 as PCT
International Application No. PCT / JP00/04711

and (if applicable) was amended on _____

I hereby stated that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclosure information known to me which is material to the examination of this application in accordance with Title 37, code of Federal Regulations, 1.56 I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing of this application:

PRIOR FOREIGN APPLICATION

Number	Country	Filing Date Day/Month/Year	Date First Laid Open or Published	Date Patented or Granted	Priority Claimed
Hei.11-200294	Japan	14/July/1999			Yes

I hereby claim the benefit under 35 U.S.C. 120/365 of all United States applications listed below and PCT International applications listed above or below, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national, or PCT International, filing date of this application:

PRIOR U.S. OR PCT APPLICATION(S)

Application No.	Day/Month/Year	Status (pending, abandoned, granted)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint the following patent agents with full power of substitution, association and revocation to prosecute this application and/or international application and to transact all business in the Patent and Trademark Office connected therewith:



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